

Procedures I and II. Surprisingly, it is seen from Table I that despite the presence of both surfactant and lithium salt in this composition at the same level as in Example 10, both the surface resistivities and charge dissipation times remained too high to qualify this ceramer as antistatic. At 21% and 30% R.H. the coatings
5 were not antistatic, while at 38% R.H. the surface resistivity was 2×10^{13} ohm/square (compared to 5×10^{10} ohm/square at 38% R.H for Example 11). In addition, the charge dissipation times at 21% and 30% R.H. for this coating were infinite, while at 38% R.H. the observed charge dissipation time was 14.6 seconds (compared to 0.5 seconds for Example 11).

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Example 14:

This example illustrates the typical chemical preparation, coating and curing of a ceramer hardcoat derived from an alkaline silica sol but lacking a surface treatment agent.

15 In a round-bottom flask I mixed 60 g Nalco 2327 alkaline silica sol and 47.6 g N,N-dimethyl acrylamide. Water was extracted using a Buchi Model 121 Rotavapor set a water-bath temperature of 60°C and a vacuum level of 90 Torr. When all the water was extracted, 20.3 g pentaerythritol triacrylate were added to the flask to obtain a crystal clear dispersion. Next, 4 g of this dispersion were
20 added to 21 g isopropyl alcohol and 0.16 g Irgacure photoinitiator to result in a 16% dispersion in isopropanol. This 16% dispersion was coated on polyester sheets and subsequently cured in exactly the same fashion as in Example 2. The cured coatings were optically clear to the naked eye. The average percent haze of the coated sheets was 1.2%.

25 Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity for 3 hours. In all three cases the charge dissipation times for the coatings were infinite, and the surface resistivities exceeded 6×10^{13} ohm/square.

Exempl 15:

This example illustrates the effect of adding both a polyalkylene oxide surfactant and perfluorinated lithium salt LiSO_3CF_3 on the properties of the cured ceramer of Example 14.

To 22.5 g of the 16% dispersion of Example 14 were added with vigorous agitation 0.3 g of a 16% solution of DOW CORNING 57 surfactant additive, next, 0.6 g of a 16% solution of lithium trifluoromethanesulfonate (LiSO_3CF_3) were added dropwise. The resulting dispersion turned milky white and the silica sol particles precipitated out of the dispersion to form a white paste at the bottom of the flask. No amount of added deionized water caused the precipitated silica to redisperse back in the liquid phase. Coatings of this milky white dispersion on polyester film according to the procedure of Example 2 resulted in an optically unacceptable hazy coating with unacceptable rough texture. The average percent haze of the coated sheets was 16.2.

Example 16:

This example illustrates the antistatic properties of a ceramer hardcoat derived from alkaline silica sol and comprising a glycidoxo-terminated coupling agent.

In a round-bottom glass flask I mixed 119 g Nalco 2327 silica sol, 12 g 3-glycidoxopropyltrimethoxysilane (Aldrich), 12 g N,N-dimethyl acrylamide, and 76.1 g pentaerythritol triacrylate. Water was extracted from this whitish mixture using a Buchi Rotavapor at a water-bath temperature of 55°C. The dispersion (residual liquid) turned crystal clear when all the water was extracted. This residual liquid weighed 146 g. I prepared a 16% dispersion of this ceramer in isopropanol by adding 4 g of this dispersion to 24 g isopropanol and 0.14 g Irgacure 184 photoinitiator. This 16% dispersion was coated on polyester sheets and subsequently cured in exactly the same fashion as in Example 2. The resulting

cured coating on the polyester sheets was optically clear to the naked eye. The average percent haze of the coated sheets was 1.1.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test
5 Procedures I and II. It was found that at all three humidity levels the surface resistivity exceeded 6×10^{13} ohm/square, which is the upper limit of measurement of the instrument used in this study. Moreover, the observed charge dissipation times at all three humidity levels were infinite. The coating of this example was therefore judged not antistatic.

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Example 17:

This example illustrates the antistatic properties of the coating of Example 16 when both polyalkylene oxide surfactant and perfluorinated lithium salt LiSO_3CF_3 are added to the composition.

15 To 22.5 g of the 16% ceramer dispersion of Example 15 were added with vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate (LiSO_3CF_3) and 0.3 g of a 16% solution of DOW CORNING 57 surfactant additive. The resulting crystal clear dispersion was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The resulting cured coating on
20 the polyester sheets was optically clear to the naked eye. The average percent haze of the coated sheets was 1.1.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their antistatic properties measured according to Test
25 Procedures I and II. It is seen from Table I that the observed surface resistivities and charge dissipation times at all three humidity levels have dropped significantly compared to the values observed in Example 16 and are in fact almost identical to the values observed in Example 3, indicating that the presence of a surface treatment agent significantly affects the antistatic properties of a cured ceramer coating.

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These examples illustrate the effect of added conventional antistatic salts on the properties of ceramer dispersions:

Example 18

5 **LiBF₄:** In a glass jar I mixed 12.3 g of the 16% ceramer dispersion of Example 2 with 0.2 g lithium tetrafluoroborate LiBF₄ (an antistatic salt used in the prior art, such as U.S. Pat. No. 4,582,781). It was found that the LiBF₄ powder precipitated immediately to the bottom of the jar and remained indefinitely insoluble in the ceramer dispersion. The addition of 2 g deionized water to this
10 inhomogeneous mixture did not cause the salt to dissolve. After 24 hours of the salt addition, the liquid phase of this inhomogeneous mixture was filtered through No. 54 Whatman filter paper and coated and cured on polyester sheets following the procedure of Example 2. The cured coating appeared to be optically clear to the naked eye. The average percent haze of the coated sheets was 1.7%.

15 Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test Procedures I and II. It was found that at all three humidity levels the surface resistivity exceeded 6×10^{13} ohm/square, which is the upper limit of measurement of the instrument used in this study. Moreover, the charge dissipation times at all
20 three humidity levels were infinite. The coating of this example was therefore judged not antistatic.

Example 19

25 **K[C₈F₁₇SO₃]:** In a glass jar I mixed 13.7 g of the 16% ceramer dispersion of Example 2 with 0.33 g of potassium perfluorinated octylsulfonate K[C₈F₁₇SO₃] (available under the trade name FC95 from 3M, St. Paul, MN). Upon addition of this salt, the previously clear ceramer dispersion turned white and the silica precipitated out of the dispersion, forming a pasty, whitish residue at the bottom of the flask. The addition of deionized water to this inhomogeneous mixture did not
30 cause the precipitated silica to redisperse in the milky white liquid phase. It was

concluded in this experiment that $K[C_8F_{17}SO_3]$ (an antistatic salt used in the prior art, such as U.S. Pat. No. 4,582,781) is not a suitable antistatic additive for the ceramer composition of this invention as it caused it to lose its chemical stability.

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Example 20

$LiCO_2CH_3$: In a glass flask I mixed 13.5 g of the 16% ceramer dispersion of Example 2 and 0.25 g lithium acetate (Aldrich) and 2 g deionized water. After a 48 hour period, the lithium acetate powder dissolved completely in the ceramer dispersion which remained optically clear. Aliquots of this dispersion were coated on polyester sheets using a #9 Myer rod as described in the coating procedure of Example 2. However, when the wet coatings were dried in the forced air oven at 60°C, a white precipitate formed in the coating and resulted in an unacceptable granular pattern on the polyester substrate indicative of the flocculation of the silica. It was concluded in this experiment that lithium acetate is not a suitable antistatic additive for the ceramer composition of this invention.

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Example 21

$NaSO_4(CH_2)_{11}CH_3$: In a glass flask containing 22.5 g of the 16% ceramer dispersion of Example 2, I added dropwise 0.6 g of a 16% solution of sodium lauryl sulfate salt in deionized water. Addition of the aqueous sodium lauryl sulfate salt, however, caused instant flocculation of the silica and its precipitation to the bottom of the holding flask where it formed an intractable paste. Subsequent coating of this inhomogeneous mixture on polyester resulted in a whitish inhomogeneous film. It was concluded in this experiment that sodium lauryl sulfate is not a suitable antistatic additive for the ceramer composition of this invention.

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Example 22

This Example illustrates the antistatic properties of a ceramer wherein the curable organic phase is derived from an organofunctional silane monomer.

In glass flask containing 25 g Nalco 2327 silica sol I added dropwise and with vigorous mixing, 21 g methyl triethoxysilane (Aldrich). The mixture turned completely homogeneous and transparent after 48 hours of mixing at 23°C. To this homogeneous dispersion I added 0.5 g $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and 0.8 g of a 50% solution of ZONYL FSN surfactant in isopropanol. The resulting mixture remained perfectly clear. Next, samples of this mixture were coated on polyester sheets using a #9 Myer rod and the coated sheets placed in a forced air oven at 99°C for 20 minutes. The resultant hardcoat was transparent, reading 1.1% haze at 23°C. The hardcoated sheets were conditioned for 3 hours at 30% and 38% relative humidity and their antistatic property measured as in Test Procedures I and II. As shown in Table I, the coatings exhibited excellent surface resistivity and charge dissipation times under both conditions.

Table I

Example	$\rho_s (\Omega/\text{cm}^2)$			CDT(sec.)			Haze.(%)	Note
	21%	30%	38%	21%	30%	38%		
1	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	0.3	bare PET
2	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	0.7	Control
3	4×10^{11}	1.9×10^{11}	6×10^{10}	1.54	0.8	0.6	1.4	Invention
4	7×10^{11}	2×10^{11}	2×10^{10}	2.3	0.9	0.6	1.3	Invention
5	-	3×10^{11}	$1.8 \times 10^{10*}$	-	0.4	0.2*	1.3	Invention
6	4×10^{11}	7×10^{11}	3×10^{11}	4.24	2.55	1.6	0.9	Invention
7	2×10^{12}	7×10^{11}	5×10^{11}	4.62	2.90	1.9	0.9	Invention
8	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.2	Control
9	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.0	Control
10	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.2	Control
11	4×10^{11}	7.3×10^{10}	5.0×10^{10}	1.6	0.6	0.5	1.4	Invention
12	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.2	Control
13	$>6 \times 10^{13}$	$>6 \times 10^{13}$	2×10^{13}	∞	∞	14.6	1.5	Control
14	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.2	Control
15	N/A**	N/A	N/A	N/A	N/A	N/A	16.2	Control
16	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.1	Control
17	5.8×10^{11}	1.9×10^{11}	6×10^{10}	1.54	0.8	0.6	1.1	Invention
18	$>6 \times 10^{13}$	$>6 \times 10^{13}$	$>6 \times 10^{13}$	∞	∞	∞	1.7	Control
19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Control

20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Control
21	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Control
22	-	6×10^{11}	4×10^{11}	-	2.6	1.8	1.1	Invention

5 * Readings taken at 51%R.H. and 23°C.

 ** N/A (Not Applicable) refers to experimental examples where the addition of
antistatic salt and/or surfactant led to the flocculation and precipitation of the silica
particles from the previously stable dispersion.

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Claims:

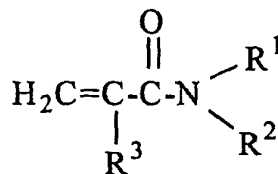
1. A cured, antistatic, ceramer coating, comprising:
 - (a) a polymeric matrix;
 - 5 (b) a plurality of surface treated, colloidal inorganic oxide particles interspersed in the matrix, wherein the colloidal inorganic oxide particles have a negative surface charge;
 - (c) an antistatic amount of an antistatic agent dispersed in the polymeric matrix, wherein the antistatic agent comprises a perfluorinated anion
 - 10 having at least one perfluorinated moiety; and
 - (d) an amount of a nonionic surfactant effective to bias the perfluorinated moiety to migrate to a surface of the polymeric matrix.
2. The antistatic coating of claim 1, wherein the composition
- 15 comprises 100 parts by weight of the polymeric matrix, 10 to 50 parts by weight of the surface treated, colloidal, inorganic oxide particles, 0.1 to 10 parts by weight of the antistatic agent, and 0.1 to 10 parts by weight of the nonionic surfactant.
3. The antistatic coating of claim 2, wherein the surface treated,
- 20 colloidal, inorganic oxide particles comprise surface treated, colloidal silica.
4. The antistatic coating of claim 2, wherein the composition further comprises a cation corresponding to the negatively surface charged inorganic oxide particles, wherein the cation is a quaternary ammonium cation.
- 25 5. The antistatic coating of claim 4, wherein the quaternary ammonium cation is NH_4^+ .
6. The antistatic coating of claim 2, wherein the polymeric matrix is
- 30 derived from a curable binder component comprising a plurality of free radically

curable monomers having an average free radically curable functionality in the range from 1.5 to 3.

7. The antistatic coating of claim 2, wherein the polymeric matrix is derived from a curable binder component comprising one or more organofunctional silane monomers.

8. The antistatic coating of claim 6, wherein said plurality of free radically curable monomers comprises an N,N-disubstituted (meth)acrylamide monomer and at least one multifunctional (meth)acrylate monomer.

9. The antistatic coating of claim 8, where the N,N-disubstituted (meth)acrylamide monomer has the formula:



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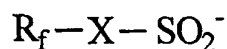
wherein R¹ and R² are each independently selected from hydrogen, an alkyl group optionally having hydroxy, halide, carbonyl, or amido functionalities, an alkylene group optionally having carbonyl and amido functionalities, an alkoxy group, an aryl group, an alkaryl group, and a heteroaryl group; with the proviso that only one of R¹ and R² is hydrogen; and R³ is hydrogen, or an alkyl group of 1 to 4 carbon atoms.

10. The antistatic coating of claim 6, wherein the colloidal inorganic oxide particles are surface treated with a coupling agent comprising a first moiety reactive with the colloidal inorganic oxide particles and a second, radiation curable moiety copolymerizable with the free radically curable monomers.

11. The antistatic coating of claim 10, wherein the colloidal inorganic oxide particles comprise silica, and the first reactive moiety is a silane moiety.

12. The antistatic coating of claim 2, wherein each perfluorinated moiety of the perfluorinated anion comprises no more than 4 carbon atoms.

13. The antistatic composition of claim 2, wherein the perfluorinated anion has the formula:



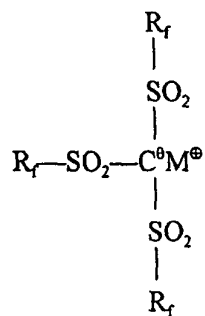
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wherein R_f is a perfluorinated group of 1 to 4 carbon atoms.

14. The antistatic coating of claim 13, wherein the coating further comprises a Li^+ counteranion corresponding to the anion.

15. The antistatic coating of claim 13, wherein R_f is $-CH_3$.

16. The antistatic coating of claim 2, wherein the antistatic agent is a methide salt of the formula:

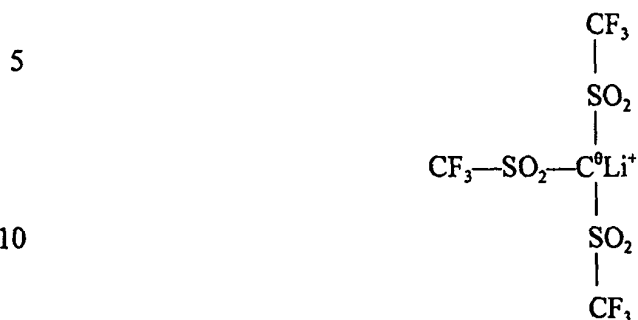


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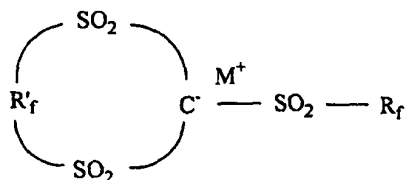
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wherein each R_f is independently a perfluorinated moiety of 1 to 4 carbon atoms; and M^+ is selected from the group consisting of Na^+ , Li^+ , quaternary ammonium, K^+ , and combinations thereof.

17. The antistatic coating of claim 16, wherein the methide salt has the formula:



18. The antistatic coating of claim 2, wherein the antistatic agent is a methide salt of the formula:

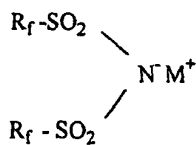


wherein R_f is a monovalent perfluorinated moiety of 1 to 4 carbon atoms; R'_f is a divalent perfluorinated moiety; and M^+ is selected from the group consisting of Na^+ , Li^+ , quaternary ammonium, K^+ , and combinations thereof.

19. The antistatic coating of claim 18, wherein M^+ is Li^+ , R_f is $-\text{CF}_3$, and R'_f is $-\text{CF}_2\text{CF}_2-$.

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20. The antistatic coating of claim 2, wherein the antistatic agent is an imide salt of the formula:

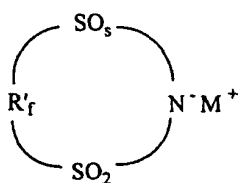


wherein each R_f is independently a perfluoro moiety of 1 to 4 carbon atoms; and M^+ is selected from the group consisting of Na^+ , Li^+ , quaternary ammonium, K^+ , and combinations thereof.

5 21. The antistatic coating of claim 20, wherein each R_f is selected from $-CF_3$ and $-C_2F_5$.

22. The antistatic coating of claim 20, wherein M^+ is Li^+ .

10 23. The antistatic coating of claim 2, wherein the antistatic agent is a methide salt of the formula:



15 wherein R'_f is a divalent perfluorinated moiety of 1 to 4 carbon atoms; and M^+ is selected from the group consisting of Na^+ , Li^+ , quaternary ammonium, K^+ , and combinations thereof.

24. The antistatic coating of claim 23, wherein R'_f is selected from
20 $-CF_2CF_2-$ and $-CF_2CF_2CF_2-$.

25. The antistatic coating of claim 23, wherein M^+ is Li^+ .

26. The antistatic coating of claim 7, wherein the nonionic surfactant
25 comprises a polyalkylene oxide moiety and a surface active moiety substantially insoluble in the free radically curable monomers.

27. The antistatic coating of claim 26, wherein the insoluble surface active moiety is selected from a perfluorinated moiety, a hydrocarbon moiety, and a polysiloxane moiety.

5 28. A radiation curable, coatable, antistatic ceramer composition comprising:

(a) a curable binder component;

(b) a plurality of surface treated, colloidal inorganic oxide particles having a negative surface charge;

10 (c) an antistatic amount of an antistatic agent dispersed in the polymeric matrix, wherein the antistatic agent comprises a perfluorinated anion comprising at least one perfluorinated moiety; and

(d) an amount of a nonionic surfactant effective to bias the perfluorinated moiety to migrate to a surface of the composition.

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29. The ceramer composition of claim 28, wherein the composition comprises 100 parts by weight of the curable binder component, 10 to 50 parts by weight of the surface treated, colloidal, inorganic oxide particles, 0.1 to 10 parts by weight of the antistatic agent, and 0.1 to 10 parts by weight of the nonionic
20 surfactant.

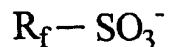
30. The ceramer composition of claim 29, wherein the surface treated, colloidal, inorganic oxide particles comprise surface treated, colloidal silica.

25 31. The ceramer composition of claim 30, wherein the composition further comprises a cation corresponding to the negatively surface charged inorganic oxide particles, wherein the cation is a quaternary ammonium cation.

32. The ceramer composition of claim 29, wherein said curable binder
30 component comprises an N,N-disubstituted (meth)acrylamide monomer and at least one multifunctional (meth)acrylate monomer.

33. The ceramer composition of claim 29, wherein each perfluorinated moiety of the perfluorinated anion comprises no more than 4 carbon atoms.

34. The antistatic composition of claim 29, wherein the perfluorinated anion has the formula:

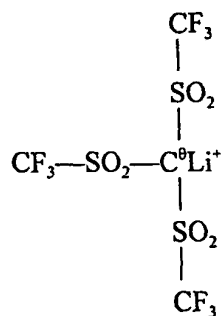


wherein R_f is a perfluorinated group of 1 to 4 carbon atoms.

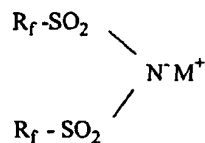
35. The antistatic coating of claim 34, wherein the coating further comprises a Li^+ countercation corresponding to the perfluorinated anion.

36. The ceramer composition of claim 34, wherein R_f is $-CF_3$.

37. The ceramer composition of claim 29, wherein the anion has the formula:



38. The ceramer composition of claim 29, wherein the antistatic agent is an imide salt of the formula:



wherein each R_f is independently a perfluoro moiety of 1 to 4 carbon atoms; and M^+ is selected from the group consisting of Na^+ , Li^+ , quaternary ammonium, K^+ , and combinations thereof.

5 39. The ceramer composition of claim 38, wherein each R_f is selected from $-CF_3$ and C_2F_5 .

40. The ceramer composition of claim 38, wherein M^+ is Li^+ .

10 41. The ceramer composition of claim 29, wherein the nonionic surfactant comprises a polyalkylene oxide moiety and a surface active moiety substantially insoluble in the free radically curable monomers.

42. A method of providing a polymeric substrate with a protective,
15 antistatic, ceramer coating comprising the steps of:

(a) coating an admixture onto the polymeric substrate, wherein
the admixture is a coatable ceramer composition comprising a plurality of surface
treated, colloidal inorganic oxide particles having a negative surface charge, a
curable binder component, a perfluorinated anion, and an amount of a nonionic
20 surfactant effective to bias the perfluorinated moiety to migrate toward a surface of
the admixture; and

(b) curing the binder component.

43. The method of claim 42, wherein the admixture further comprises
25 an amount of a solvent sufficient to provide the admixture with a coatable
viscosity, and the method further comprises the step of substantially drying the
coated substrate before the curing step.

44. The method of claim 42, wherein the coatable admixture further
30 comprises a quaternary ammonium cation corresponding to the negatively charged
surface treated, colloidal inorganic oxide particles.

45. The method of claim 42, wherein the composition comprises 100 parts by weight of the binder component, 10 to 50 parts by weight of the surface treated, colloidal, inorganic oxide particles, 0.1 to 10 parts by weight of the antistatic agent, and 0.1 to 10 parts by weight of the nonionic surfactant.

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46. The method of claim 45, wherein the surface treated, colloidal, inorganic oxide particles comprise surface treated, colloidal silica.

47. The method of claim 45, wherein the composition further comprises
10 a cation corresponding to the negatively surface charged inorganic oxide particles, wherein the cation is NH_4^+ .

48. The method of claim 45, wherein each perfluorinated moiety of the perfluorinated anion comprises no more than 4 carbon atoms.

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49. The antistatic coating of claim 48, wherein the coating further comprises a Li^+ countercation corresponding to the perfluorinated anion.

50. A composite structure, comprising

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(a) a polymeric substrate having a coatable surface;

(b) an antistatic ceramer coating provided on the coatable surface, wherein the coating comprises

(i) a polymeric matrix;

(ii) a plurality of surface treated, colloidal inorganic oxide
25 particles interspersed in the matrix, wherein the colloidal inorganic oxide particles have a negative surface charge;

(iii) an antistatic amount of an antistatic agent dispersed in the polymeric matrix, wherein the antistatic agent comprises a perfluorinated anion having at least one perfluorinated moiety; and

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(iv) an amount of a nonionic surfactant effective to bias the perfluorinated moiety to migrate to a surface of the polymeric matrix.

51. The composite structure of claim 50, wherein the composition comprises 100 parts by weight of the polymeric matrix, 10 to 50 parts by weight of the surface treated, colloidal, inorganic oxide particles, 0.1 to 10 parts by weight of the antistatic agent, and 0.1 to 10 parts by weight of the nonionic surfactant.

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52. The composite structure of claim 51, wherein the surface treated, colloidal, inorganic oxide particles comprise surface treated, colloidal silica.

53. The composite structure of claim 51, wherein the composition
10 further comprises a cation corresponding to the negatively surface charged inorganic oxide particles, wherein the cation is a quaternary ammonium cation.

54. The composite structure of claim 53, wherein the quaternary ammonium cation is NH_4^+ .

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55. The composite structure of claim 51, wherein each perfluorinated moiety of the perfluorinated anion comprises no more than 4 carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/14213

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/00 C08K13/06 //(C08K13/06,5:00,9:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 36669 A (MINNESOTA MINING & MFG) 21 November 1996 cited in the application see claims 1-11	1-55
A	WO 95 16547 A (MINNESOTA MINING & MFG) 22 June 1995 see claims 1,2,5,11	1-55

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

13 October 1998

Date of mailing of the international search report

23/10/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

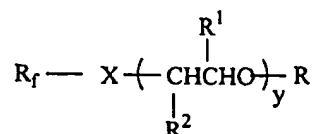
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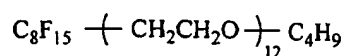
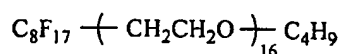
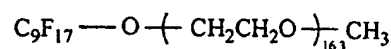
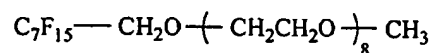
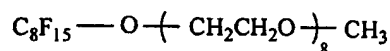
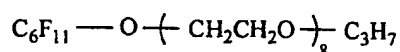
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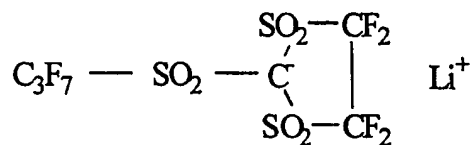
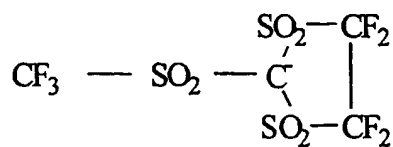
of such moieties include perfluorinated moieties having a sufficient number of carbon atoms, e.g., 5 or more, so as to be insoluble in the curable binder, a polysiloxane moiety, a hydrocarbon moiety having 8 to 20 carbon atoms, combinations of these, and the like.

- 5 Examples of nonionic surfactants incorporating a polyalkylene oxide and an insoluble perfluorinated moiety (nonionic perfluoro surfactant) may be represented by the following formula:

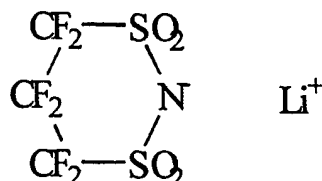
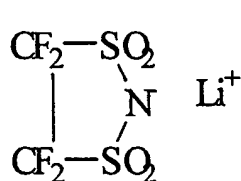
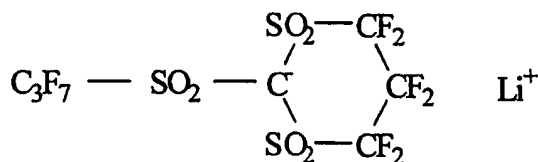


- 10 wherein R_f includes a perfluorinated moiety such as a perfluoroalkyl group, a perfluoroalkylene group, a perfluorocycloalkyl group, a perfluoroalkoxy group, and a perfluorocycloalkylene group having from 5 to 16 carbon atoms, X can be any divalent linking group such as $-\text{O}-$, $-\text{SO}_2\text{NR}^3-$, $-\text{CONR}^4-$, $-\text{CH}_2\text{O}-$,
 15 or a single bond; R , R^1 , R^2 , R^3 , and R^4 are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms; and y is a number from 6 to 60, preferably 6 to 30. A particularly preferred class of nonionic perfluoro surfactants is the ZONYL family of surfactants available from E.I. duPont de Nemours and Company under the designations "FSN", "FSO", "FSP", "VR", and the like. Other useful nonionic
 20 perfluoro surfactants are listed below:





5



10 The ceramer compositions of the present invention further incorporate a nonionic surfactant. Preferred nonionic surfactants comprise both a surface active moiety which is insoluble in the curable binder component as well as a polyalkylene oxide moiety. Generally, the polyalkylene oxide moiety contains a plurality of repeating units of the formula $-(R^5O)-$, wherein each $-R^5O-$ is

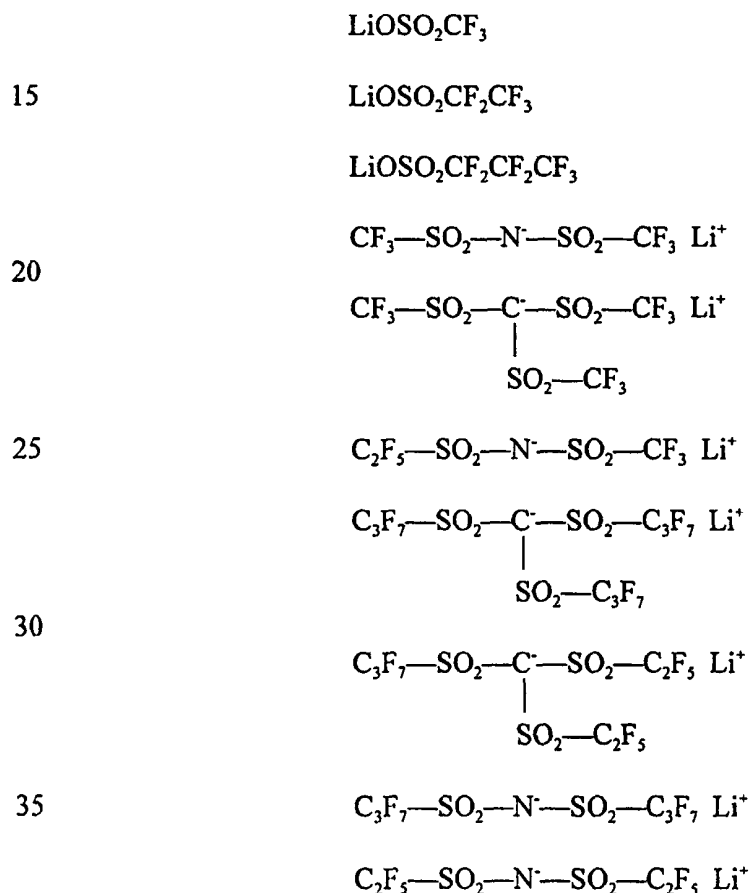
15 independently a divalent alkylene oxide moiety of 1 to 6, preferably 1 to 3 carbon atoms. Examples of such moieties include methylene oxide, ethylene oxide, propylene oxide, combinations of these, and the like. Preferably, such repeating units comprise ethylene oxide, $-\text{CH}_2\text{CH}_2\text{O}-$, as a repeating unit in that a

20 solvent for the counter cations, especially Li^+ , of the perfluorinated anion. Desirably, the nonionic surfactant includes 6 to 60 of such repeating units.

The insoluble moiety of the nonionic surfactant may be any moiety which is sufficiently insoluble in the curable binder component such that the moiety tends to seek out the surface of the curable binder component. Representative examples

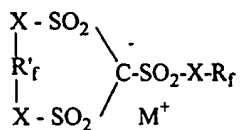
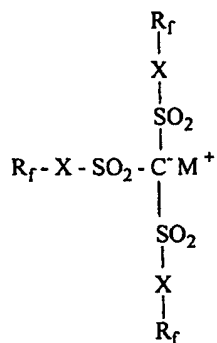
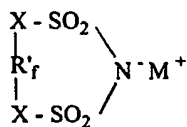
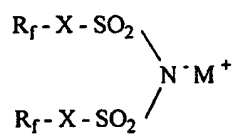
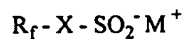
wherein each R_f is independently a monovalent perfluorinated moiety of 1 to 4 carbon atoms; each R'_f is independently a divalent perfluorinated group; each X is independently a divalent linking group such as oxygen or a single bond; and each M^+ is independently selected from Na^+ , K^+ , Li^+ , quaternary ammonium such as NH_4^+ , combinations of these, and the like. Preferably, each R_f is CF_3 -, each R'_f is $-CF_2CF_2-$ or $-CF_2CF_2CF_2-$, and each M is Li^+ . A description of perfluorinated sulfonyl containing salts and their synthesis can be found in U.S. Pat. Nos. 4,505,997, 5,021,308, 5,072,040, 5,162,177, and 5,273,840.

Specific examples of perfluoroalkyl sulfonates, perfluoroalkylsulfonyl imides or perfluoroalkylsulfonyl methides including Li^+ cations are illustrated below. However, the present invention is not limited to the following examples:



faster than salts including one of the other cations. Such salts are also much more compatible with other ingredients of the composition.

One class of salts of a perfluorinated anion found to be particularly suitable in the practice of the present invention comprises perfluorinated sulfonyl containing salts. Perfluorinated sulfonyl containing salts may be represented by compounds of the following formulae:



trialkoxysilane, perfluoromethyl alkyl trialkoxy silane, perfluoro alkyl trichlorosilane, and mixtures thereof.

Although any surface treatment agent may be used, it is preferred that the colloidal inorganic oxide particles are surface treated with a coupling agent such that the colloids are (meth)acrylate functionalized in those embodiments in which the curable binder component is radiation curable. Advantageously, the functionalized particles can copolymerize with the radiation curable binder component when the ceramer composition is exposed to a curing dosage of radiation such as heat, visible light, ultraviolet light, or electron beam radiation. Typically, in the case of colloidal silica particles, the silica particles are functionalized by adding a silyl(meth)acrylate to an aqueous sol of colloidal silica. Examples of preparing acrylate functionalized colloidal silica are described in U.S. Patent Nos. 4,491,508 and 4,455,205 to Olsen et al.; U.S. Patent Nos. 4,478,876 and 4,486,504 to Chung; and U.S. Patent No. 5,258,225 to Katsamberis.

Generally, the antistatic agent comprises a salt of a perfluorinated anion comprising at least one perfluorinated moiety such as a perfluoroalkyl, perfluoroalkoxy, and/or perfluoroalkylene moiety. The size of the perfluoro moiety or moieties, as the case may be, may dramatically affect the performance of the antistatic agent. Preferably, therefore, each perfluorinated moiety of the perfluorinated anion includes no more than 1 to 4 carbon atoms to ensure that the anion does not destabilize the colloids and cause flocculation. Examples of such compact monovalent and divalent perfluorinated moieties include CF_3^- , CF_3CF_2^- , $-\text{CF}_2\text{CF}_2^-$, $-\text{CF}_2\text{CF}_2\text{CF}_2^-$, CF_3O^- , combinations of these, and the like. Most preferably, any perfluoroalkyl moiety is CF_3^- , any perfluoroalkoxy moiety is CF_3O^- , and any perfluoroalkylenemoiety is $-\text{CF}_2^-$ or $-\text{CF}_2\text{CF}_2^-$.

The salt of the perfluorinated anion further comprises a counteranion effective to neutralize the negative electrical charge associated with the anion. Examples of suitable counteranions include Na^+ , K^+ , Li^+ , quaternary ammonium such as NH_4^+ , combinations of these, and the like. Preferably, the cation is Li^+ in that salts including Li^+ as the counteranion help dissipate static charges substantially

with the surface treated charged colloids. Salts of perfluorinated anions can be used with surface treated charged colloids without causing flocculation, especially when the perfluorinated moieties of the salts are sufficiently compact such that the perfluorinated moieties of the salts are soluble in the curable binder component. In contrast, if the perfluoro moieties are too big, then flocculation may occur and the ceramer composition could, as a result, lose its desired optical and rheological properties. Particularly, optical clarity and low viscosity characteristics could be adversely affected. Also, an oily film may form on the surface of the resultant coating.

While not wishing to be bound by theory, it is believed that surface treatment of the colloidal inorganic oxide particles enhances the dispersibility of the particles in ceramer compositions because, in practical effect, the surface treatment coats the particle surfaces, thereby protecting those surfaces and adding steric bulk (i.e., a spacing layer) around the particles. Surface treatment thus makes it more difficult for the antistatic agent to adversely interact with the particles. Surface treatment generally involves reacting a sol containing the colloidal particles with a surface treatment agent such that the surface treatment agent interacts with and bonds to the surfaces of the particles. This procedure will be described and illustrated below, particularly in the Examples.

Any surface treatment agent capable of interacting with the surfaces of the colloidal inorganic oxide particles may be used with beneficial results. Preferred surface treatment agents are hydrolyzable organofunctional silane compounds. Such compounds are also referred to as "silane coupling agents". Examples of silane coupling agents suitable for this invention include acryloxyalkyl trimethoxysilane, methacryloxyalkyl trimethoxysilane, (meth)acryloxyalkyl triethoxysilane, (meth)acryloxyalkyl trichlorosilane, phenyl trichlorosilane, phenyl trimethoxysilane, phenyl triethoxysilane, vinyl trimethoxysilane, vinyl triethoxysilane, vinyl trichlorosilane, methyl trimethoxysilane, methyl triethoxysilane, propyl trimethoxysilane, propyl triethoxysilane, glycidoxymethyl trimethoxysilane, glycidoxymethyl triethoxysilane, glycidoxymethyl trichlorosilane, perfluoro alkyl

interspersed throughout the interior volume of the coating, provide not only surface channels, but also internal channels for dissipating static charges.

Generally, a negative surface charge is provided by using a sol having an appropriate pH. For example, in those embodiments of the invention in which the colloidal inorganic oxide particles are silica or tin oxide derived from an aqueous sol, a negative surface charge is assured when the sol has a pH greater than 7, preferably greater than 8, and more preferably greater than 9.

A variety of cations can be used in the sol to counter the negatively surface charged colloids. Examples of such cations include Na^+ , K^+ , Li^+ , a quaternary ammonium cation such as NR_4^+ , wherein each R may be any monovalent moiety, but is preferably H or CH_3 , combinations of these, and the like. Preferably, however, the cation is quaternary ammonium such as NH_4^+ in that quaternary ammonium is a much better electrical conductor than the other listed cations. Resultant anhydrous ceramer compositions including quaternary ammonium also tend to be more stable over time than compositions including the other cations. Further, coatings prepared from compositions including quaternary ammonium as a counter cation for the silica particles provide substantially better antistatic protection as compared to coatings incorporating the other cations. In preferred embodiments, the improvement is many orders of magnitude. Further, ceramer compositions including quaternary ammonium and a nonaqueous solvent (the preparation of such compositions will be described below) tend to have better optical clarity, i.e., higher light transmittance, as compared to other cations. To achieve such advantages, NH_4^+ , for example, may be provided quite easily merely by adding NH_4OH to the sol. Advantageously, NH_4OH not only serves as a source of NH_4^+ , but it also helps provide the sol with a basic pH.

The negatively charged, colloidal, inorganic oxide particles tend to be very sensitive to other charges in the ceramer composition. Because of this sensitivity, it has been very difficult to identify any kind of ionic antistatic agents that can be used in combination with the charged colloids without causing the colloids to flocculate. It has now been discovered, however, that surface treating the colloids and using an antistatic agent that is a salt of perfluorinated anions in combination provides a system in which the anionic antistatic agent is unexpectedly extremely compatible

colloidal particles include water, aqueous alcohol solutions, lower aliphatic alcohols, toluene, ethylene glycol, dimethyl acetamide, formamide, and combinations thereof. The preferred liquid medium is water. When the colloidal particles are dispersed in water, the particles are stabilized on account of common electrical charges on the surface of each particle. The common electrical charges tend to promote dispersion rather than agglomeration, because the similarly charged particles repel one another, thereby preventing aggregation. By contrast, in the powder state, such as in fumed silica or silica gel, uncharged colloidal particles will agglomerate to form networks and thus will not provide a uniform dispersion of particles when combined with the organic components of the ceramer compositions. Preferred ceramers are easily distinguished from otherwise similar compositions that comprise agglomerated colloidal inorganic oxide particles. When the sol-derived colloidal inorganic oxide particles in a ceramer are replaced with the same weight fraction of agglomerated colloidal inorganic oxide particles, wetted powder results.

Sols useful in the practice of the present invention may be prepared by methods well known in the art. Suitable sols are also commercially available. For example, colloidal silicas dispersed as sols in aqueous solutions are commercially available under the tradename "NALCO" (Nalco Chemical Co., Oak Brook, Ill.). Examples include NALCO 2327, NALCO 1040, NALCO 1060, NALCO 1030, NALCO 1115, and the like.

The colloidal inorganic oxide particles of the present invention are characterized as having a negative surface charge, which is balanced by a suitable counter cation. Advantageously, negatively charged colloids and the antistatic agent described herein are a synergistic combination that provides ceramer coatings with superior antistatic capabilities. While not wishing to be bound by theory, a possible rationale to explain the synergy between the negatively surface charged colloids and the salts of perfluorinated anions can be suggested. In many of the previously known antistatic coatings, channels for dissipating static charge are located primarily on the surfaces of such coatings. In contrast, it is believed that the negatively charged colloids and salts of perfluorinated anions of the present invention, which are

pentamethacrylic acid esters of aliphatic pentols such as adonitol; the hexaacrylic acid and hexamethacrylic acid esters of hexanols such as sorbitol and dipentaerythritol; the diacrylic acid and dimethacrylic acid esters of aromatic diols such as resorcinol, pyrocatechol, bisphenol A, and bis(2-hydroxyethyl) phthalate; 5 the trimethacrylic acid ester of aromatic triols such as pyrogallol, phloroglucinol, and 2-phenyl-2,2-methylolethanol; and the hexaacrylic acid and hexamethacrylic acid esters of dihydroxy ethyl hydantoin; and mixtures thereof.

One combination of free radically curable monomers found to be particularly suitable in the practice of the present invention for making tough, 10 abrasion resistant, impact resistant, optically clear antistatic coatings is a formulation including about 1 part by weight of a monofunctional N,N disubstituted (meth)acrylamide (such as N,N-dimethyl (meth)acrylamide) and about 6 parts by weight of one or more multifunctional, free radically curable monomers (such as an admixture of di, tri, and tetra functional, free radically 15 curable monomers derived from pentaerythritol and commercially available under the trade designation "SR444" from Sartomer Co., West Chester, Pennsylvania).

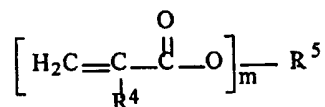
Colloidal inorganic oxide particles of the present invention are preferably non-aggregated particles, desirably substantially spherical in shape, characterized by an average particle diameter of about 5 nm to about 1000 nm, more preferably 10 nm 20 to 50 nm. These size ranges facilitate ease of dispersion of the particles into coatable compositions and provide coatings that are smoothly surfaced and optically clear. Average particle size of the colloids can be measured using transmission electron microscopy to count the number of particles of a given diameter.

A wide range of colloidal inorganic oxide particles could be used in the 25 present invention. Representative examples include silica and metal oxides such as alumina, tin oxide, iron oxide, zirconia, vanadia, titania, and the like, with silica being most preferred.

The colloidal inorganic oxide particles useful in preparing ceramers for use in this invention most desirably are provided as a sol rather than as a powder or a gel. 30 In the sol state, the colloidal inorganic oxide particles are dispersed in a liquid medium. Representative examples of liquid media suitable as dispersants for the

compounds, corresponding multifunctional isocyanates could be used in place of the triisocyanate, respectively.

A preferred class of multifunctional (meth)acryl functional compounds includes one or more multifunctional, ethylenically unsaturated esters of (meth)acrylic acid and may be represented by the following formula:



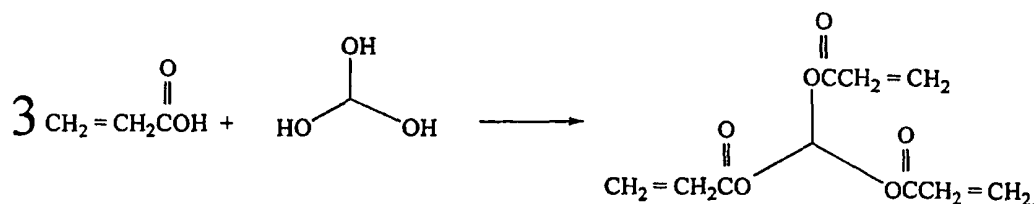
wherein R^4 is hydrogen, halogen or a $(\text{C}_1\text{-C}_4)$ alkyl group; R^5 is a polyvalent organic group having m valencies and can be cyclic, branched, or linear, aliphatic, aromatic, or heterocyclic, having carbon, hydrogen, nitrogen, nonperoxidic oxygen, sulfur, or phosphorus atoms; and m is an integer designating the number of acrylic or methacrylic groups in the ester and has a value of 2 to 7. Preferably, R^4 is hydrogen, methyl, or ethyl, R^5 has a molecular weight of about 14-100, and m has a value of 2-6. More preferably, m has a value of 2-5, most preferably 3-4.

Where a mixture of multifunctional acrylates and/or methacrylates are used, m preferably has an average value of about 1.05 to 3.

Specific examples of suitable multifunctional ethylenically unsaturated esters of (meth)acrylic acid are the polyacrylic acid or polymethacrylic acid esters of polyhydric alcohols including, for example, the diacrylic acid and dimethylacrylic acid ester of aliphatic diols such as ethyleneglycol, triethyleneglycol, 2,2-dimethyl-1,3-propanediol, 1,3-cyclopentanediol, 1-ethoxy-2,3-propanediol, 2-methyl-2,4-pentanediol, 1,4-cyclohexanediol, 1,6-hexamethylenediol, 1,2-cyclohexanediol, 1,6-cyclohexanedimethanol; the triacrylic acid and trimethacrylic acid esters of aliphatic triols such as glycerin, 1,2,3-propanetrimethanol, 1,2,4-butanetriol, 1,2,5-pentanetriol, 1,3,6-hexanetriol, and 1,5,10-decanetriol; the triacrylic acid and trimethacrylic acid esters of tris(hydroxyethyl) isocyanurate; the tetraacrylic and tetramethacrylic acid esters of aliphatic triols, such as 1,2,3,4-butanetetrol, 1,1,2,2-tetramethylolethane, 1,1,3,3-tetramethylolpropane, and pentaerythritol tetraacrylate; the pentaacrylic acid and

commercially available from a number of different suppliers. Alternatively, such compounds can be prepared using a variety of well known reaction schemes. For example, according to one approach, a (meth)acrylic acid or acyl halide or the like is reacted with a polyol having at least two, preferably 2 to 6, hydroxyl groups.

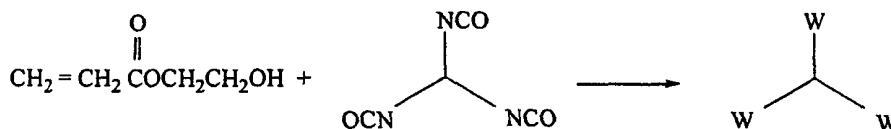
- 5 This approach can be represented by the following schematic reaction scheme which, for purposes of illustration, shows the reaction between acrylic acid and a triol:



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This reaction scheme as illustrated provides a trifunctional acrylate. To obtain di, tetra, penta, or hexa functional compounds, corresponding diol, tetrols, pentols, and hexols could be used in place of the triol, respectively.

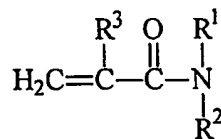
- 15 According to another approach, a hydroxy or amine functional (meth)acrylate compound or the like is reacted with a polyisocyanate, or isocyanurate, or the like having 2 to 6 NCO groups or the equivalent. This approach can be represented by the following schematic reaction scheme which, for purposes of illustration, shows the reaction between hydroxyethyl acrylate and
- 20 a triisocyanate:



wherein each W is $-\overset{\text{O}}{\parallel}\text{NHCCH}_2=\text{CH}_2$. This reaction scheme as illustrated provides a

25 trifunctional (meth)acrylate. To obtain di, tetra, penta, or hexa functional

The N,N-disubstituted (meth)acrylamide monomers generally have the formula:



wherein R¹ and R² are each independently hydrogen, a (C₁-C₈)alkyl group (linear, branched, or cyclic) optionally having hydroxy, halide, carbonyl, and amido functionalities, a (C₁-C₈)alkylene group optionally having carbonyl and amido functionalities, a (C₁-C₄)alkoxymethyl group, a (C₄-C₁₈)aryl group, a (C₁-C₃)alk(C₄-C₁₈)aryl group, or a (C₄-C₁₈)heteroaryl group; with the proviso that only one of R¹ and R² is hydrogen; and R³ is hydrogen, a halogen, or a methyl group. Preferably, R¹ is a (C₁-C₄)alkyl group; R² is a (C₁-C₄)alkyl group; and R³ is hydrogen, or a methyl group. R¹ and R² can be the same or different. More preferably, each of R¹ and R² is CH₃, and R³ is hydrogen.

Examples of such suitable (meth)acrylamides are N-(3-bromopropionamidomethyl) acrylamide, N-tert-butylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-(5,5-dimethylhexyl)acrylamide, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-(hydroxymethyl)acrylamide, N-(isobutoxymethyl)acrylamide, N-isopropylacrylamide, N-methylacrylamide, N-ethylacrylamide, N-methyl-N-ethylacrylamide, N-(fluoren-2-yl)acrylamide, N-(2-fluorenyl)-2-methylacrylamide, 2,3-bis(2-furyl)acrylamide, N,N'-methylenebis acrylamide. A particularly preferred (meth)acrylamide is N,N-dimethyl (meth)acrylamide.

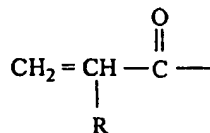
Other examples of free radically curable monomers include alkenes such as ethene, 1-propene, 1-butene, 2-butene (cis or trans) compounds including an allyloxy moiety, and the like.

In addition to the monofunctional free radically curable monomer, any kind of multifunctional free radically curable monomers preferably having di, tri, tetra, penta, and/or hexa free radically curable functionality also can be used in the present invention. Such multifunctional (meth)acrylate compounds are

(meth)acrylate, (meth)acrylonitrile, β -cyanoethyl-(meth)acrylate, 2-cyanoethoxyethyl (meth)acrylate, p-cyanostyrene, p-(cyanomethyl)styrene, an ester of an α,β -unsaturated carboxylic acid with a diol, e.g., 2-hydroxyethyl (meth)acrylate, or 2-hydroxypropyl (meth)acrylate; 1,3-dihydroxypropyl-2-
5 (meth)acrylate; 2,3-dihydroxypropyl-1-(meth)acrylate; an adduct of an α,β -unsaturated carboxylic acid with caprolactone; an alkanol vinyl ether such as 2-hydroxyethyl vinyl ether; 4-vinylbenzyl alcohol; allyl alcohol; p-methylol styrene, (meth)acryloyloxyethyl trimethyl ammonium chloride, (meth)acrylamidopropyl trimethylammonium chloride, vinylbenzyl
10 trimethylammonium chloride, 2-hydroxy-3-allyloxypropyl trimethylammonium chloride, (meth)acryloyloxypropyl dimethylbenzylammonium chloride, dimethylaminoethyl (meth)acrylate, vinylbenzyl trimethylammonium chloride, N-(3-sulfopropyl)-N-(meth)acryloyloxyethyl-N,N-dimethylammonium betaine, 2-
[(meth)acryloyloxy]ethyl trimethylammonium methosulfate, N-(3-sulfopropyl)-N-
15 (meth)acrylamidopropyl-N, N-dimethylammonium betaine, N,N-dimethylamino (meth)acrylate, (meth)acryloyloxyethyl acid phosphate, (meth)acrylamidopropyl sodium sulfonate, sodium styrene sulfonate, styrene sulfonic acid, (meth)acrylic acid, maleic acid, fumaric acid, maleic anhydride, vinyl sulfonic acid, 2-
(meth)acrylamide-2-methyl-1-propanesulfonic acid, maleic anhydride, mixtures
20 thereof, and the like.

A particularly preferred class of monofunctional free radically curable monomers suitable in the practice of the present invention includes one or more N,N-disubstituted (meth)acrylamides. Use of an N,N-disubstituted (meth)acrylamide provides numerous advantages. For example, the use of this
25 kind of monomer provides antistatic coatings which show improved adhesion to polycarbonate substrates. Further, use of this kind of monomer also provides coatings with improved weatherability and toughness. Preferably, the N,N-disubstituted (meth)acrylamide has a molecular weight in the range from 99 to about 500, preferably from about 99 to about 200, in order to minimize the
30 tendency, if any, of the inorganic oxide particles to flocculate and precipitate out of the ceramer composition.

- which a carbon-carbon double bond is directly or indirectly linked to an aromatic ring. Examples of such compounds include styrene, alkylated styrene, alkoxy styrene, free radically curable naphthalene, alkylated vinyl naphthalene, alkoxy vinyl naphthalene, combinations of these, and the like. Another representative
- 5 class of monofunctional, free radically curable monomers includes compounds in which a carbon-carbon double bond is attached to an cycloaliphatic, heterocyclic, and/or aliphatic moiety such as 5-vinyl-2-norbornene, 4-vinyl pyridine, 2-vinyl pyridine, 1-vinyl-2-pyrrolidinone, 1-vinyl caprolactam, 1-vinylimidazole, N-vinyl formamide, and the like.
- 10 Another representative class of such monofunctional free radically curable monomers include (meth)acrylate functional monomers that incorporate moieties of the formula:



- 15 wherein R is a monovalent moiety, such as hydrogen, halogen, methyl, or the like. Representative examples of such monomers include (meth)acrylamides, chloro(meth)acrylamide, linear, branched, or cycloaliphatic esters of (meth)acrylic acid containing from 1 to 20, preferably 1 to 8, carbon atoms, such as methyl
- 20 (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate; vinyl esters of alkanolic acids wherein the alkyl moiety of the alkanolic acids contain 2 to 20, preferably 2 to 4, carbon atoms and may be linear, branched, or cyclic; isobornyl (meth)acrylate; vinyl acetate; allyl (meth)acrylate, and the like.
- 25 Such (meth)acrylate functional monomers may also include other kinds of functionality such as hydroxyl functionality, nitrile functionality, epoxy functionality, carboxylic functionality, thiol functionality, amine functionality, sulfonyl functionality, combinations of these, and the like. Representative examples of such free radically curable compounds include glycidyl

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 4/52, C07C 2/54, C08F 2/38, 10/00	A1	(11) International Publication Number: WO 95/21872 (43) International Publication Date: 17 August 1995 (17.08.95)
(21) International Application Number: PCT/GB95/00253 (22) International Filing Date: 9 February 1995 (09.02.95) (30) Priority Data: 9402612.7 10 February 1994 (10.02.94) GB (71) Applicant (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ABDUL-SADA, Ala'a, K. [IQ/GB]; 77 Ashdown, Eaton Road, Hove Sussex BN3 3AR (GB). SEDDON, Kenneth, Richard [GB/GB]; 26 Ormonde Park, Belfast BT10 0LS (GB). STEWART, Nevin, John [GB/GB]; 16 Scillonian Road, Guildford, Surrey GU2 5PS (GB). (74) Agent: KRISHNAN, Suryanarayana, Kalyana; BP International Limited, Patents & Agreements Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IONIC LIQUIDS (57) Abstract This invention relates to an ionic liquid comprising a ternary melt of (a) a compound of the formula: R_nMX_{3-n} wherein R is a C_1 - C_6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1, or 2; (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide; and (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide. These ionic liquids can be used as catalysts for the oligomerization or polymerization of olefins and also for the alkylation of paraffins, isoparaffins and aromatics with olefins.		

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IONIC LIQUIDS

This invention relates to novel ionic liquids and to the use thereof as the reaction medium and catalyst for various chemical reactions such as eg producing olefin polymers, especially butene polymers from raffinates I and II from a refining process and which
5 contain *inter alia* a mixture of butene-1, butene-2 and iso-butene.

Ionic liquids are primarily mixtures of salts which melt below room temperature. Such salt mixtures include aluminium halides in combination with one or more of imidazolium halides, pyridinium halides or phosphonium halides and the latter being preferably
10 substituted. Examples of the latter include one or more of 1-methyl-3-butyl imidazolium halides, 1-butyl pyridinium halide and tetrabutyl phosphonium halides.

It is known to use these ionic liquids as solvents and as catalysts for eg the dimerization and /or oligomerization of olefins
15 such as ethylene, propylene, butene-1 and/or butene-2 and for the alkylation of benzene using alkyl halides. In this context Jeffrey A Boon et al states in an article in the Journal of Organic Chemistry, Vol 51, 1986, pp 480-483 that:

"Completely ionic liquids are not the usual solvent for organic
20 reactions. Most ionic liquids are liquid only at high temperatures and offer little advantage over the more commonly used aqueous or organic media. Most work on organic reactions in molten salts have employed eutectic mixtures, but they still require temperatures above 200°C."

25 This article further goes on to state that:

"Numerous other substituted imidazolium and pyridinium chlorides form molten salts with aluminium chloride but do not possess the favourable physical properties we sought for this investigation."

5 From the above, it is clear that not all ionic liquids possess the properties desirable for specific reactions in which they are to be used and that the choice of specific ionic liquids for a given reaction is far from straightforward.

10 A further article by Yves Chauvin et al in J Chem Soc, Chem Comm, 1990, pp 1715-1716 also emphasises this point. In this article, the authors intend to carry out catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts to the exclusion of all other products. Moreover, the authors state that:

15 "However, it seems that no attempt has been made to take advantage of the solubility of the organometallic catalyst and the insolubility of the reaction products of the catalytic reaction in these solvents."

The authors add that:

20 "In the absence of any nickel complex, acidic melts catalyse the formation of oligomers, the molecular weight of which is characteristic of a cationic reaction".

To further add to the unpredictability of these reactions, French Patent No. 2611700 (Institut Francais du Petrole) describes a
25 process for the oligomerization of olefins including *inter alia* butene-1 and butene-2 using a nickel catalyst in the liquid phase; the catalyst used is specifically a nickel complex dissolved in an ionic liquid, the latter being the liquid phase.

30 More recently, FR-A-2626572 describes a process for alkylation using as catalyst an ionic liquid comprising at least one halide of aluminium or boron and at least one quaternary ammonium halide. The quaternary ammonium halide can be a dialkyl imidazolium halide.

From the above it will be clear that the function of ionic liquids in these reactions is far from predictable. Furthermore,
35 none of the publications referred to above disclose ionic liquids

comprising alkyl substituted imidazolium halides in which any of the alkyl substituents has more than 4 carbon atoms.

It has now been found that ternary melts comprising a mixture of various quaternary ammonium halides and aluminium halides perform very well as ionic liquid catalysts.

Accordingly, the present invention is an ionic liquid which comprises a ternary melt of:

- (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
 - (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
 - (c) at least one of hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide.
- The compound (a) in the ternary melt is suitably an aluminium halide or a gallium halide, such as aluminium trichloride or gallium trichloride, or, an alkyl aluminium/gallium halide such as an alkyl aluminium/gallium dihalide or a dialkyl aluminium/gallium halide, and is preferably ethyl aluminium/gallium dichloride.
- The component (b) in the ionic liquid is at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide. These may be suitably selected from 1-alkyl-3-alkyl imidazolium halides and 1-alkyl pyridinium halides. Specific examples of these compounds include the following: 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, 1-methyl-3-hexyl imidazolium chloride, 1-methyl-3-octyl imidazolium chloride, 1-methyl-3-decyl imidazolium chloride, 1-methyl-3-dodecyl imidazolium chloride, 1-methyl-3-hexadecyl imidazolium chloride, 1-methyl-3-octadecyl imidazolium chloride, ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene pyridinium dibromide, ethylene pyridinium dichloride, butyl pyridinium chloride and benzyl pyridinium bromide.

As will be appreciated, in the case of a symmetrical molecule

such as a 1,3-disubstituted imidazolium halide, it would be possible to interchange the position of the substituents in the 1- and 3-positions or to have each of the substituents in the 1- and 3-positions with 5 or more carbon atoms in the alkyl group.

- 5 Furthermore, it would also be possible to have the chloride ion in the compounds listed above interchanged with bromide or iodide ions to produce compounds which are equally effective as ionic liquids.

A feature of the present invention is that where the chain length of at least one of the alkyl chains in the imidazolium halide, especially the alkyl chain in the 3-position, is greater than 4
10 carbon atoms, the catalytic activity of ionic liquids comprising such halides is increased for polymerization reactions with respect to alkyl chains having 4 carbon atoms or less in that higher molecular weight products are obtained where this is desirable. The
15 performance of such ionic liquids is particularly superior when the feedstock being polymerised is a raffinate I, raffinate II or isobutene.

The component (c) in the ternary melts of the present invention is at least one of a hydrocarbyl-substituted quaternary ammonium
20 halide and a hydrocarbyl-substituted phosphonium halide. Of the substituent groups in the ammonium halides at least one substituent is an alkyl group. The other substituents may be the same or different groups selected from hydrogen, alkyl, aryl, aralkyl and alkaryl groups. Similarly, the hydrocarbyl substituted phosphonium
25 halides contain at least one hydrocarbyl group. The other substituents may be the same or different groups selected from hydrogen, alkyl, aryl, aralkyl and alkaryl groups. Specific examples of such compounds include *inter alia* the tetra alkyl ammonium or phosphonium halides, especially those in which the alkyl group has 1-
30 18 carbon atoms.

The ternary melts of the present invention are suitably prepared by mixing the components in an atmosphere inert under the reaction conditions as described in our published EP-A-0558187. It is preferable to purify each of the components in the melt prior to
35 preparing the melt. Thus, aluminium trichloride can be purified by

repeated sublimations until the melt at the bottom of the sublimator is clear and the aluminium trichloride takes on a lustrous, shiny appearance; the hydrocarbyl substituted imidazolium or pyridinium halides can be purified by repeated recrystallisations from solutions thereof in a suitable solvent; and the hydrocarbyl substituted quaternary ammonium or phosphonium halide can be purified by dissolving the halide in a suitable solvent such as eg ethanol and precipitation of the halide from the ethanol solution by dilution with eg diethyl ether followed by filtration and drying in an inert atmosphere.

Ionic liquids comprising the ternary melts of the present invention can be used in any of the reactions in which ionic liquids in general are capable of acting as a catalytic component. Thus for instance, the ionic liquids of the present invention can be used eg for alkylation and polymerisation reactions.

Where these ionic liquids are used as catalysts for the alkylation reaction, this may be either the alkylation of isoparaffins such as isobutane with a C2-C4 olefin such as eg ethylene, to produce alkylates which enhance the octane rating of fuels, or, for the alkylation of aromatics with an olefins such as eg the conversion of benzene to ethyl benzene with a view to producing styrene therefrom. The alkylation reaction is suitably carried out at a temperature of eg below 100°C, suitably from -30 to +50°C. The ratio of the catalytic ionic liquid phase to the hydrocarbon phase used for alkylation would largely depend upon the reactivity of the olefin and the acidity of the particular ionic liquids chosen. As a general guide the mole ratio of catalyst to olefins is suitably in the range from 1000 : 1 to 1 : 1000. In terms of the volume ratio of catalyst phase to hydrocarbon phase, this would suitably be in the range from in the range from 100 : 1 to 1 : 100, and more preferably from 20 : 1 to 1 : 20.

Where an iso-paraffin is being alkylated with an olefin, the ratio of iso-paraffins to olefin is suitably in the range from 1000 : 1 to 1 : 1000

Thus, according to a further embodiment, the present invention

is a process for the polymerization of an olefinic feedstock comprising one or more of C2-C4 olefins, said process comprising bringing the feedstock into contact with an ionic liquid comprising a ternary melt of:

- 5 (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
 - (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
 - 10 (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide
- such that the melting point of the ionic liquid is below the reaction temperature.

15 The components (a), (b) and (c) can be the same and have the same characteristics as those described above in respect of the ternary melts of the present invention described above.

The polymerization products referred to herein are meant to include:

- 20 i. oligomers which are conventionally defined as "a very low molecular weight polymer in which the number of repeating units equals 2-10" (see Polymer Chemistry, An Introduction by R B Seymour and C E Carraher, 2nd Edition, 1988, p 14, and published by Marcel Dekker Inc), and
- 25 ii. polymers which have at least 11 repeating units, ie an average molecular weight of 600 to 100,000.

The hydrocarbon feedstock for this process is suitably ethylene, propylene, butene-1, butene-2 and/or isobutene but is preferably a raffinate from the refining process and can be raffinate I or raffinate II.

30 Raffinate I is usually the butadiene raffinate which is a by-product formed during the thermal or catalytic cracking (whether or not fluid) operation in a refinery and principally comprises C4 hydrocarbons especially a mixture of butene-1, butene-2 and isobutene along with some saturated hydrocarbons. More specifically,

35 such raffinate I comprises at least 10% w/w of iso-butene, from 20-

40% w/w of butene-1 and butene-2, and from 10-20% w/w of butanes.

Raffinate II is the unpolymerised by-products recoverable when Raffinate I is subjected to polymerization using eg Lewis acid catalysts or the by-product gases resulting from the production of the lead-free anti-knock compound, methyl tertiary butyl ether (MTBE). In both processes the by-products have substantially the same composition and are rich in n-butenes. These by-products are the so called "raffinate II" and typically contain from 30-55% w/w of butene-1, about 10% w/w of cis-butene-2, about 17% w/w of trans-butene-2, upto 6% w/w of iso-butene and upto 30% w/w of the saturated C4 hydrocarbons n-butane and iso-butane. Since raffinate II, an otherwise wasted material, is capable of being cationically polymerized to polybutenes, its value as raw material is readily apparent.

The relative ratios of the two components (a), (b) and (c) in the ionic liquid should be such that they are capable of remaining in the liquid state under the reaction conditions. Typically, the relative mole ratio of compound (a) to the components [(b) + (c)] in the ionic liquid is suitably in the range from 1 : 2 to 3.0 : 1, preferably from 1.5 : 1 to 2 : 1. Within this range, where the ionic liquid is intended for use as a reaction medium or a solvent, the amount of the component (a) can be less than 50 mole % of the total ionic liquid. However, where the ionic liquid is intended for use as a catalyst, the amount of component (a) is preferably greater than 50 mole % of the total ionic liquid. The relative mole ratios of (b) : (c) is suitably in the range from 0.01 : 1 bearing in mind that within this range the ratios chosen should be such that the resultant ionic liquid should be a liquid at room temperature.

The polymerization reaction is suitably carried out at a temperature from -50°C to +100°C, preferably from -30°C to +70°C. The reaction can be carried out either:

- (i) by bubbling the olefinic hydrocarbon feedstock to be polymerized through the ionic liquid, or,
- (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and

then subjecting such a dispersion to polymerization.

In the case of (i), the rate at which the olefinic hydrocarbon feedstock is to be bubbled and in the case of (ii), the amount of ionic liquid mixed with the feedstock and, in both cases the reaction
5 temperature used will depend upon the molecular weight of the product desired. Normally in this type of reaction one would expect that the higher the temperature used, the lower the molecular weight of the polymer formed.

Irrespective of the nature of the reaction in which such ionic
10 liquids are used as catalysts, eg oligomerization, polymerisation, alkylation or isomerisation, the reaction pressures used should be such that the components of the ionic liquid remain in the liquid phase during the reaction.

It has now been found that, surprisingly, when any of the
15 processes, especially oligomerization, polymerisation or alkylation is used, the reaction product forms a separate phase from the ionic liquid. This product phase is substantially free of any catalyst or ionic liquid contaminants. The product can thus be readily separated from the ionic liquid eg by tapping. This feature has
20 several advantages:

A. Ease of separation of the product polymer from the catalytic component means that further undesirable reactions eg of the olefinic end-group in the polymer, such as eg isomerization, is minimised thereby retaining the structure of the polymer formed. This also
25 means that such further undesirable reactions are avoided without resort to the use of conventional reaction quenching agents such as aqueous alkali.

B. The product formed need not be water-washed because of the relatively low levels of the catalytic ionic liquid in the product
30 thereby avoiding a process step.

C. The ease of separation of the product from the ionic liquid catalyst means that the catalyst can be recycled and thereby reduces operational costs.

If process (ii) is used, it may be necessary to add a quenchant
35 such as aqueous ammonia in order to terminate the reaction and/or to

neutralise any catalytic components. The products can then be water-washed and the product polymer separated. In this case, the unreacted material can be allowed to evaporate and the dried product isolated.

5 A further feature of the present invention is that this method enables a much higher percentage of n-butenes to be incorporated in the product polymer than would be possible in conventional cationic polymerization processes using eg aluminium trichloride or boron trifluoride.

10 Yet another surprising feature of the present process is that contrary to expectations, the molecular weight of the polymer product does not increase with decreasing temperatures. In spite of using reaction temperatures which are substantially higher than those used in the prior art, the present process gives rise to polymers which
15 have a higher molecular weight than the oligomers formed by said prior art processes.

These surprising features give a very desirable outlet for relatively low value feedstocks such as raffinates I and II at the same time making maximum use of the reactive carbon values in that
20 feedstock and hence reducing the wastage of any hydrocarbon values in such feedstock.

The polymer products produced by the process of the present invention can be used eg as lubricants or cutting fluids in the industry without further treatment. Alternatively, these polymers
25 can be maleinised and converted to corresponding succinic anhydride derivatives which in turn can be converted into the corresponding imide which is a detergent for lube oils and fuels.

The present invention is further illustrated with reference to the following Examples. In Tables below, the intensity referred to
30 is the peak height which corresponds to the number of protons in that position. In this respect the notations very strong, strong, medium and weak represent the following range of peak intensities (I/I₀):

very strong	-	80-100
strong	-	60-80
35 medium	-	40-60

weak	-	20-40
very weak	-	<20
δ (ppm)	-	chemical shift in parts per million

5 EXAMPLE 1:

A. Purification of aluminium trichloride:

In an inert-atmosphere box, anhydrous aluminium trichloride (ca. 200 g) was placed in a sublimator with sodium chloride (2 g) and powdered aluminium (1 g). The apparatus was transferred to a vacuum
10 line where the mixture was heated *in vacuo* in a silicone oil-bath, to 150°C. The aluminium trichloride was left to sublime until ca. 10% of it remained at the bottom of the sublimator together with the molten NaCl and impurities. After cooling, the apparatus was placed
15 back into the inert-atmosphere box where the sublimed AlCl_3 was removed by scraping and then placed again into a clean apparatus with NaCl (2 g) for re-sublimation. (Powdered aluminium was utilized in the first sublimation only, to remove iron impurities). Five successive sublimations were carried out until the melt observed at the bottom of the sublimator was clear and the AlCl_3 took on a
20 lustrous, shiny appearance.

B. Preparation of 1-ethyl-3-methylimidazolium chloride:

The preparation was carried out in a fume cupboard. The apparatus comprised a round-bottomed flask provided with an additional funnel and was adapted to be heated to elevated
25 temperature. The apparatus was purged clean with nitrogen and the reaction was carried out under nitrogen. 1-Methylimidazole (300 ml), which had previously been distilled *in vacuo* over KOH, was placed in the flask under nitrogen. Acetonitrile (ca. 150 ml, distilled over CaH_2) was then added to the flask. The mixture was then heated
30 slowly in small increments until the internal temperature of the flask was 68°C and then allowed to stabilize for one day. The nitrogen purge was then replaced with a stream of ethyl chloride which was administered through a flow meter at the rate of 2 dm³ ethyl chloride per hour for two days. Thereafter, the flow of ethyl
35 chloride was reduced to 1 dm³ per hour and maintained at this rate

for a further three days. After this duration, a solution containing the desired product was removed from the flask whilst still hot by cannula and this solution was extracted with ethyl acetate and small white crystals of 1-ethyl-3-methylimidazolium chloride were recovered from the extract. Further purification was carried out by recrystallisation from aliquots of ethyl ethanoate.

C. Purification of tetra-ethylammonium chloride:

Tetra-ethylammonium chloride (100 g) was dissolved in ethanol (150 ml). Diethyl ether was then added to this solution until tetra-ethylammonium chloride started to precipitate. The solution was cooled to -13°C and left at this temperature overnight. The resulting crystals were filtered under dry nitrogen and then heated in a Schlenk round bottomed flask to 100°C under vacuum for 48 hours. The resulting solid was then transferred to a dry box ready to use.

D. Preparation of Ternary melt:

Crystalline 1-ethyl-3-methylimidazolium chloride was melted in vacuo and poured into an aluminium foil "boat" under an inert atmosphere and then allowed to solidify therein. The solid so formed was then broken into large lumps. These lumps were then reacted with lumps of tetraethyl ammonium chloride and aluminium trichloride in varying quantities and under conditions shown in the Table 1 below to prepare six different batches (Batch Nos. 1-6) of acidic and basic melts. Lumps were used instead of powders to prevent charring of the melt during heating.

TABLE 1

Batch No.	[Et ₄ N]Cl (g)	[MeEtim]Cl (g)	AlCl ₃	Ternary Melt (g)	AlCl ₃ (Moles)
1	0.8922 (23.333%)	0.3936 (11.66%)	2.0	3.287	0.65
2	0.6958 (17.5%)	0.5922 (17.5%)	2.0	3.288	0.65
3	1.2428 (40%)	0.5498 (20%)	1.0	2.793	0.40
4	0.6214 (20%)	1.0996 (40%)	1.0	2.721	0.40
5	0.3107 (10%)	1.3745 (50%)	1.0	2.680	0.40
6	0.1553 (5%)	1.512 (55%)	1.0	2.667	0.40

[Et₄N]Cl is tetra-ethylammonium chloride

[MeEtim]Cl is 1-ethyl-3-methylimidazolium chloride

Ternary melt is [Et₄N]Cl/[MeEtim]Cl/AlCl₃

The ternary melts were characterised using ¹H NMR spectroscopy by placing the neat ionic liquid in a 4mm diameter NMR tube *in vacuo*.

- 5 No solvent was used for the analysis. The results of the analysis are tabulated in Tables 2 (standard melt) 3 and 4 (ternary melt) below:

TABLE 2

¹H NMR of Standard Binary C₁/C₂ Melt for Comparison

10

δ(ppm)	Intensity (I/I ₀)	Type
1.0	strong	triplet
3.4	very strong	triplet
3.8	medium	doublet
6.9	medium	doublet
7.8	medium	singlet

TABLE 3

¹H NMR of Ternary Melt (65% AlCl₃, 23.3% [Et₄N]Cl & 11.7% [MeEtim]Cl)

δ(ppm)	Intensity (I/I ₀)	Type
0.7	very strong	singlet
1.0	weak	singlet
2.6	very strong	singlet
3.3	medium	singlet
3.7	weak	doublet
4.6	very weak	singlet
6.8	very weak	doublet
7.8	very weak	singlet

[Et₄N]Cl - tetra ethyl ammonium chloride

- 15 [MeEtim]Cl - 1-ethyl-3-methyl imidazolium chloride

TABLE 4

¹H NMR of Ternary Melt (40% AlCl₃, 15% [Et₄N]Cl & 45% [MeEtim]Cl)

δ(ppm)	Intensity (I/I _o)	Type*
1.0	very strong	singlet
2.8	very weak	singlet
3.5	very strong	singlet
3.8	strong	singlet
7.4	medium	singlet
9.2	weak	singlet

* - all peaks were broad peaks

[Et₄N]Cl - tetraethyl ammonium chloride

5 [MeEtim]Cl - 1-ethyl-3-methyl-imidazolium chloride

EXAMPLE 2:

An ionic liquid was prepared in an inert atmosphere glove box consisting of three components, ie tetraethyl ammonium chloride (2.96g), 1-ethyl-3-methyl imidazolium chloride (9.17g) and aluminium

10 trichloride (22.33g) in a mole ratio of 0.08 : 0.25 : 0.67 by the process described in our published EP-A-0558187. 5ml of the ternary melt ionic liquid so formed was dispersed into 200g of raffinate I feedstock (having an olefinic composition shown in Table 5 below) in 750 ml of heptane with stirring at atmospheric pressure and at 10°C

15 for a duration of 180 minutes. The reaction was exothermic but a temperature rise of no greater than 10°C was observed during the reaction period. The yield of the polymer product was 68.5% wt/wt based on the weight of olefin present, ie 114.95 g of polymer product was obtained from 167.9g of olefin. The number average molecular

20 weight of the polymer, Mn, was 1000.

TABLE 5

Raffinate I Feedstock Olefin	% wt/wt Concentration
Iso-butene	46.0
Butene-1	25.0
Trans-butene-2	8.2
Cis-butene-2	2.8
Saturated hydrocarbons	remainder

Comparative Test not according to the invention:

For comparison, an ionic liquid was prepared according to the process of Example 1 above but now consisting of 1-ethyl-3-methyl-imidazolium chloride (12.2g) and aluminium trichloride (22.3g). The components were present in the same mole ratio (A) : (b) of 2:1 and the polymerisation of raffinate I of the composition in Table 4 above was carried out in an identical fashion to that in Example 2 above. The yield of the polymer product in this case was 71.3g (42.5% w/w on olefin in the feed) and the number average molecular weight of the polymer, Mn, was 1000, ie the same as of the polymer in Example 2 above.

These results demonstrate that the use of a ternary melt ionic liquid as catalyst increases the rate of polymerisation of the monomer from 42.5% w/w of olefin fed (Comparative test) to 68.5% w/w of olefin (according to the invention).

Claims:

1. An ionic liquid comprising a ternary melt of
 - (a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2,
 - 5 (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted pyridinium halide, and
 - (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide.
2. An ionic liquid according to Claim 1 wherein the compound (a)
10 is aluminium trichloride, gallium trichloride or ethyl aluminium dichloride.
3. An ionic liquid according to Claim 1 or 2 wherein the hydrocarbyl imidazolium halide is a 1,3-dialkyl imidazolium halide.
4. An ionic liquid according to Claim 3 wherein at least one of
15 the alkyl groups in the hydrocarbyl substituted imidazolium halide has more than 4 carbon atoms.
5. An ionic liquid according to any one of the preceding Claims 1-4 wherein the hydrocarbyl imidazolium halide is selected from the group consisting of: 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-
20 3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, 1-methyl-3-hexyl imidazolium chloride, 1-methyl-3-octyl imidazolium chloride, 1-methyl-3-decyl imidazolium chloride, 1-methyl-3-dodecyl imidazolium chloride, 1-methyl-3-hexadecyl
25 imidazolium chloride and 1-methyl-3-octadecyl imidazolium chloride.

6. An ionic liquid according to Claim 1 or 2 wherein the hydrocarbyl pyridinium halide is 1-alkyl pyridinium halide.
7. An ionic liquid according to Claim 1, 2 or 6 wherein the hydrocarbyl pyridinium halide is selected from the group consisting of: ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene pyridinium dibromide, ethylene pyridinium dichloride, butyl pyridinium chloride and benzyl pyridinium bromide.
8. An ionic liquid according to any one of the preceding Claims wherein the component (c) in the ternary melt is at least one of a tetraalkyl ammonium halide and a tetraalkyl phosphonium halide
9. An ionic liquid according to Claim 8 wherein the component (c) in the ternary melt has 1-18 carbon atoms in each alkyl group.
10. A process for the conversion of olefinic hydrocarbons said process being selected from the group consisting of oligomerization, alkylation and polymerization in the presence of an ionic liquid catalyst which has melting point below the process temperature, wherein the ionic liquid comprises (a) an aluminium halide or a gallium halide, (b) at least one of a hydrocarbyl substituted imidazolium halide and a hydrocarbyl substituted phosphonium halide and (c) at least one of a hydrocarbyl substituted quaternary ammonium and a hydrocarbyl substituted phosphonium halide according to any one of the preceding Claims 1-9.
11. A process according to Claim 10 said process comprising polymerization of an olefinic hydrocarbon feedstock comprising one or more of C2-C4 olefins.
12. A process according to Claim 11 wherein the relative mole ratios of components (a), (b) and (c) in the ionic liquid catalyst are such that (a) : [(b) + (c)] is in the range from 1 : 2 to 3 : 1 and (b) : (c) is in the range from 0.01:1 and wherein said catalyst has a melting point below the process temperature.
13. A process according to any one of the preceding Claims 10-12 wherein the olefinic hydrocarbon feedstock for polymerization comprises ethylene, propylene, butene-1, butene-2 and/or isobutene.
14. A process according to any one of the preceding Claims 10-13 wherein the olefinic hydrocarbon feedstock is a raffinate from a

refinery process selected from raffinate I or raffinate II.

15. A process according to any one of the preceding Claims 11-14 wherein the polymerization reaction is carried out at a temperature from -50°C to +100°C.

5 16. A process according to any one of the preceding Claims 11-15 wherein the reaction is carried out either:

(i) by bubbling the olefinic hydrocarbon feedstock to be polymerized through the ionic liquid, or,

10 (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and then subjecting such a dispersion to polymerization.

17. A process according to Claim 10 wherein olefinic hydrocarbon is used for alkylation of paraffins, isoparaffins or aromatics to form alkylates.

15 18. A process according to Claim 17 wherein the alkylation reaction is that of alkylating aromatics and is carried out at a temperature of eg below 100°C, suitably from -30 to +50°C.

19. A process according to Claim 21 wherein the mole ratio of the ionic liquid to the olefinic hydrocarbon used for alkylation is in
20 the range from 1000 : 1 to 1 : 1000.

20. A process according to any one of the preceding Claims 17-19 wherein the aromatic hydrocarbon alkylated is benzene or toluene.

21. A process according to Claim 17 wherein during the alkylation of an iso-paraffin, the mole ratio of iso-paraffins to olefin is in
25 the range from 1000 : 1 to 1 : 1000.

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PCT/GB 95/00253

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/52 C07C2/54 C08F2/38 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 448 445 (INSTITUT FRANCAIS DU PETROLE) 25 September 1991 see claims 1-20 ---	1-21
A	EP,A,0 558 187 (BP CHEMICALS LTD.) 1 September 1993 see claims 1-10 ---	1, 10, 16
A	FR,A,2 611 700 (INSTITUT FRANCAIS DU PETROLE) 9 September 1988 cited in the application see page 2, line 18 - line 31; claims 1-10 -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 June 1995

Date of mailing of the international search report

10.07.95

Name and mailing address of the ISA

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EP-A-0448445	25-09-91	FR-A- 2659871 JP-A- 4217633 US-A- 5104840	27-09-91 07-08-92 14-04-92
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FR-A-2611700	09-09-88	NONE	

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 5/00, C08K 13/06 // (C08K 13/06, 5:00, 9:00)	A1	(11) International Publication Number: WO 99/02611 (43) International Publication Date: 21 January 1999 (21.01.99)
(21) International Application Number: PCT/US98/14213 (22) International Filing Date: 8 July 1998 (08.07.98) (30) Priority Data: 08/891,564 11 July 1997 (11.07.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: BILKADI, Zayn; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: BUSSE, Paul, W. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: BR, CA, CN, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ANTISTATIC CERAMER HARDCOAT COMPOSITION WITH IMPROVED ANTISTATIC CHARACTERISTICS (57) Abstract The present invention relates to an approach for improving the compatibility of antistatic agents and ceramer hardcoats so that such hardcoats can be provided with excellent antistatic characteristics. In particular, it has been discovered that the antistatic agents of this invention can be combined with aqueous sols of surface treated, colloidal inorganic oxide particles having a negative surface charge without destabilizing the negatively charged colloids. It has further been discovered that the combination of the antistatic agent and negatively charged, surface treated colloids of this invention interspersed in a cured ceramer matrix unexpectedly provides dramatic improvements in antistatic protection. The antistatic approach of this invention also provides excellent antistatic protection over a wide range of relative humidity, including conditions in which R.H. is below 40 %, especially at 15 % to 40 % R.H.		

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ANTISTATIC CERAMER HARDCOAT COMPOSITION WITH IMPROVED ANTISTATIC CHARACTERISTICS

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FIELD OF THE INVENTION

This invention relates to an antistatic protective coating and method for making the same. More particularly, the invention relates to an antistatic protective coating incorporating negatively charged inorganic oxide particles, a salt of a perfluorinated anion, and a surfactant.

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BACKGROUND OF THE INVENTION

Thermoplastic and thermosetting polymers are used to form a wide variety of structures for which optical clarity, i.e., good light transmittance, is a desired characteristic. Examples of such structures include camera lenses, eyeglass lenses, binocular lenses, retroreflective sheeting, automobile windows, building windows, train windows, boat windows, aircraft windows, vehicle headlamps and taillights, display cases, eyeglasses, watercraft hulls, road pavement markings, overhead projectors, stereo cabinet doors, stereo covers, furniture, bus station plastic, television screens, computer screens, watch covers, instrument gauge covers, optical and magneto-optical recording disks, and the like. Examples of polymer materials used to form these structures include thermosetting or thermoplastic polycarbonate, poly(meth)acrylate, polyurethane, polyester, polyamide, polyimide, phenoxy, phenolic resin, cellulosic resin, polystyrene, styrene copolymer, epoxy, and the like.

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Many of these thermoplastic and thermosetting polymers have excellent rigidity, dimensional stability, transparency, and impact resistance, but unfortunately have poor abrasion resistance. Consequently, structures formed from these materials are susceptible to scratches, abrasion, and similar damage.

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To protect these structures from physical damage, a tough, abrasion resistant "hardcoat" layer may be coated onto the structure. Many previously

known hardcoat layers have been formed from radiation curable prepolymers such as (meth)acrylate functional monomers. Such hardcoat compositions have been described, for example, in Japanese patent publication JP02-260145, U.S. Pat. Nos. 5,541,049, and 5,176,943. One particularly excellent hardcoat composition is described in WO 96/36669 A1. This publication describes a hardcoat formed from a "ceramer" used, in one application, to protect the surfaces of retroreflective sheeting from abrasion. As defined in this publication, a ceramer is a composite (preferably transparent) having inorganic oxide particles, e.g., silica, of nanometer dimensions dispersed in a crosslinkable mixture.

10 Thermoplastic polymers and thermosetting polymers, as well as hardcoats formed from such polymers, are poor electrical conductors. As a consequence, static charge can build-up on structures and coatings formed from these materials. Static charge attracts dust, which impairs optical clarity and appearance. Even the ceramer hardcoat compositions of WO 96/36669 A1 are susceptible to static charge build up. It has been desirable, therefore, to use antistatic agents to help prevent and/or dissipate static charges.

There are two common approaches for using antistatic agents with a hardcoat. One approach involves coating an antistatic agent directly onto the hardcoat layer. This approach, however, generally does not provide long-lasting antistatic protection in that such coatings tend to be easy to wipe or wear away. Another approach involves pre-mixing antistatic agents with the uncured hardcoat composition before the hardcoat is coated onto its substrate and cured. Generally, effective antistatic agents incorporated into hardcoat compositions have included one or more components in which at least one of the components is ionic. For example, U.S. Pat. No. 5,176,943 describes an antistatic agent including a combination of ionic and nonionic perfluorinated compounds.

Unfortunately, ceramers tend to be incompatible with many ionic compounds, including ionic antistatic compounds. The incompatibility arises from the preferred way in which ceramers are formed. Many ceramers are derived from aqueous sols of inorganic colloids in which the colloids are extremely charge sensitive. Adding ionic ingredients to such sols tends to destabilize the colloids,

causing the colloids to flocculate and precipitate out of the dispersion. Flocculation is not conducive to forming high quality antistatic coatings. Firstly, flocculation results in local accumulations of particles, and these accumulations are large enough to scatter light. This detracts from optical clarity. Additionally, the accumulations of particles may cause nibs and/or other defects in the resultant coatings. Abrasion resistance may also be impaired. It would be desirable, therefore, to provide an approach in which antistatic agents could be incorporated into ceramer hardcoat compositions without causing the inorganic colloids to flocculate.

Relative humidity (RH) can affect the performance of antistatic coatings. For example, some antistatic systems might perform adequately at relatively high relative humidity, e.g. $RH \geq 40\%$, yet perform dismally at relatively low relative humidity, e.g., $RH < 40\%$. Accordingly, there is also a need for antistatic systems that retain antistatic properties over wider ranges of relative humidity, particularly for conditions below 40% RH.

SUMMARY OF THE INVENTION

The present invention relates to an approach for improving the compatibility of antistatic agents and ceramer hardcoats so that such hardcoats can be provided with excellent antistatic characteristics. In particular, it has been discovered that the antistatic agents of this invention can be combined with aqueous sols of surface treated, colloidal inorganic oxide particles having a negative surface charge without destabilizing the negatively charged colloids. It has further been discovered that the combination of the antistatic agent and negatively charged, surface treated colloids of this invention interspersed in a cured ceramer matrix unexpectedly provides dramatic improvements in antistatic protection. The antistatic approach of this invention also provides excellent antistatic protection over a wide range of relative humidity, including conditions in which RH is below 40%, especially at 15% to 40% RH, preferably 20% to 40% RH.

In one aspect, the present invention relates to a cured, anti-static ceramer coating, comprising:

- (a) a polymeric matrix;
- (b) a plurality of surface treated, colloidal, inorganic oxide particles interspersed in the polymeric matrix, wherein the colloidal inorganic oxide particles have a negative surface charge;
- (c) an antistatic amount of an antistatic agent dispersed in the polymeric matrix, wherein the antistatic agent comprises a perfluorinated anion having at least one perfluorinated moiety; and
- 10 (d) an amount of a nonionic surfactant effective to bias the perfluorinated moiety to migrate to a surface of the polymeric matrix.

In another aspect, the present invention relates to a substrate bearing an antistatic ceramer coating of the type described above.

In another aspect, the present invention relates to a coatable, radiation curable, antistatic, ceramer composition comprising:

- 15 (a) a curable binder component which is preferably a plurality of copolymerizable, free radically curable monomers and/or one or more silane monomers;
- (b) a plurality of surface treated, colloidal, inorganic oxide particles having a negative surface charge;
- 20 (c) an antistatic amount of an antistatic agent, wherein the antistatic agent comprises a salt of a perfluorinated anion having at least one perfluorinated moiety; and
- (d) an amount of a nonionic surfactant effective to bias the
- 25 perfluorinated moiety to migrate to a surface of the composition.

In another aspect, the present invention relates to a method of providing a polymeric substrate with a protective, cured, antistatic ceramer coating comprising the steps of:

- (a) coating an admixture onto the polymeric substrate, wherein the
- 30 admixture is a coatable ceramer composition comprising a plurality of surface treated, colloidal, inorganic oxide particles having a negative surface charge, a

curable binder component which is preferably a plurality of copolymerizable, free radically curable monomers and/or one or more silane monomers, an antistatic amount of a perfluorinated anion having at least one perfluorinated moiety, and an amount of a nonionic surfactant effective to bias the perfluorinated moiety to
5 migrate to a surface of the admixture; and

(b) curing the curable binder component.

As used herein with respect to the present invention, the following shall apply:

“Sol” shall refer to a colloidal dispersion of substantially non-aggregated,
10 inorganic oxide particles in a liquid medium;

“Ceramer composition” shall refer to a coatable dispersion comprising substantially non-aggregated, colloidal inorganic oxide particles dispersed in a curable binder composition, wherein curing of the binder is understood to mean in a broad sense the process of solidification (hardening) of the binder brought about
15 by a suitable approach such as cooling of a molten thermoplastic material, drying of a solvent-containing composition, chemical crosslinking of a thermosetting composition, radiation curing of a radiation curable composition, or the like;

“Ceramer coating” shall refer to a coating of a ceramer composition in which the curable composition is cured to form a solid, substantially non-flowing
20 material; and

“Curable” shall mean that a coatable material can be transformed into a solid, substantially non-flowing material by means of cooling (to solidify hot melts), heating (to dry and solidify materials in a solvent), chemical crosslinking, radiation crosslinking, or the like.

25

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the
30 following detailed description. Rather the embodiments are chosen and described

so that others skilled in the art may appreciate and understand the principles and practices of the present invention.

One preferred antistatic ceramer coating embodiment of the present invention is prepared from a ceramer composition comprising a curable binder component; a plurality of inorganic oxide particles; an antistatic agent which is a salt of a perfluorinated anion; and a nonionic surfactant, each of which will be described in more detail below. A wide range of amounts of these materials may be incorporated into the composition with beneficial results. As one example of a formulation suitable for forming tough, abrasion resistant, impact resistant, optically clear, antistatic, protective, ceramer coatings, the ceramer composition may include about 100 parts by weight of the curable binder component, about 10 to 50 parts by weight of the surface treated inorganic oxide particles, about 0.1 to about 10 parts by weight of the antistatic agent, and about 0.1 to about 10 parts by weight of the nonionic surfactant. More preferably, the composition includes about 100 parts by weight of the curable binder component, about 25 to 40 parts by weight of the surface treated inorganic oxide particles, about 0.5 to about 5 parts by weight of the antistatic agent, and about 0.5 to about 5 parts by weight of the nonionic surfactant.

As one option, the curable binder component can be selected from any curable thermoplastic or thermosetting polymer such as a polyurethane, polycarbonate, polyester, polyamide, polyimide, phenoxy, phenolic resin, cellulosic resin, polystyrene, styrene copolymer, poly(meth)acrylate, epoxy, silicone resin, combination of these, and the like. As another option, the curable binder component can be in the form of prepolymeric materials which can be copolymerized or homopolymerized in situ after the composition has been coated onto a substrate.

As one example of an approach using prepolymeric materials, the curable binder component may comprise one or more partially hydrolyzed organofunctional silane monomers. Such partially hydrolyzed organofunctional silane monomers generally are capable of crosslinking upon drying and heating to form a polymeric siloxane-type matrix.

A wide variety of organofunctional silane monomers may be used in the practice of the present invention. Representative examples include methyl trimethoxysilane, methyl triethoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, a silyl (meth)acrylate, (meth)acryloxyalkyl trimethoxysilane, (meth)acryloxyalkyl trichlorosilane, phenyl trichlorosilane, vinyl trimethoxysilane, vinyl triethoxysilane, propyl trimethoxysilane, propyl triethoxysilane, glycidoxymethyl trimethoxysilane, glycidoxymethyl triethoxysilane, glycidoxymethyl trichlorosilane, perfluoro alkyl trialkoxysilane, perfluoromethyl alkyl trialkoxysilane, perfluoroalkyl trichlorosilane, combinations of these, and the like.

10 In those embodiments of the invention in which the inorganic oxide particles are surface treated with a silane coupling agent (as will be described below), such coupling agent may be the same or different from the silane monomers used to form the polymeric matrix.

As another example of an approach using prepolymeric materials, the curable binder component comprises one or more free radically curable monomers, oligomers, polymers, or combinations of these having pendant free radically curable functionality which allows the materials to polymerize and/or crosslink using thermal energy or another source of curing radiation such as electron beam radiation, ultraviolet radiation, visible light, and the like. Preferred free radically curable monomers, oligomers, and/or polymers each include one or more free-radically polymerizable, carbon-carbon double bonds such that the average functionality of such materials is greater than one free-radically carbon-carbon double bond per molecule. Materials having such moieties are capable of copolymerization and/or crosslinking with each other via such carbon-carbon double bond functionality.

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Generally, the term "monomer" as used herein refers to a single, one unit molecule capable of combination with itself or other monomers to form oligomers or polymers. The term "oligomer" refers to a compound that is a combination of 2 to 20 monomers. The term "polymer" refers to a compound that is a combination of 21 or more monomers.

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Generally, compositions including oligomeric and/or polymeric free radically curable materials tend to have higher viscosities than compositions including only free radically curable monomers. Accordingly, in applications involving techniques such as spin coating or the like in which it is desirable for the composition to have a low viscosity, e.g., a viscosity of less than 200 centipoise measured at 25°C using a Brookfield viscometer with any suitable spindle operated at a spindle speed in the range from 20 to 50 rpm, it is preferred that at least 50%, by weight, more preferably substantially all, of the prepolymers are free radically curable monomers.

Free radically curable monomers suitable in the practice of the present invention are preferably selected from combinations of mono, di, tri, tetra, penta, and hexafunctional free radically curable monomers. Various amounts of the mono, di, tri, tetra, penta, and hexafunctional free radically curable monomers may be incorporated into the present invention, depending upon the desired properties of the final coating. For example, in order to provide coatings with higher levels of abrasion and impact resistance, it is desirable for the composition to include one or more multifunctional free radically curable monomers, preferably at least both di and tri functional free radically curable monomers, such that the free radically curable monomers incorporated into the composition have an average free radically curable functionality per molecule of greater than 1. Preferred compositions of the present invention may include 1 to 35 parts by weight of monofunctional free radically curable monomers, 0 to 75 parts by weight of difunctional free radically curable monomers, 1 to 75 parts by weight of trifunctional free radically curable monomers, 0 to 75 parts by weight of tetrafunctional free radically curable monomers, 0 to 75 parts by weight of pentafunctional free radically curable monomers, and 0 to 75 parts by weight of hexafunctional free radically curable monomers, subject to the proviso that the free radically curable monomers have an average functionality of greater than 1, preferably 1.1 to 4, more preferably 1.5 to 3.

One representative class of monofunctional free radically curable monomers suitable in the practice of the present invention includes compounds in